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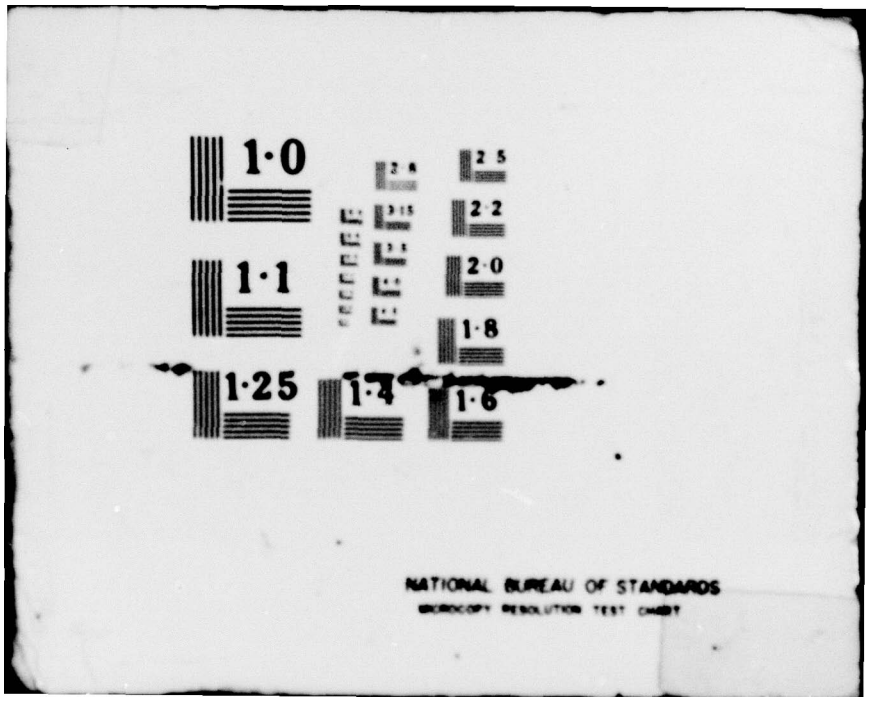
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Photochemical Transients of Electrode Bound Methylene Blue

by

C. E. Baumgartner, G. T. Marks,
H. H. Richtol and D. A. Aikens

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A 520 nm transient was observed as the result of the interaction of methylene blue triplet with methylene blue bound to an electrode surface. The transient was observed by laser flash photolysis in an outgassed thin layer transparent electrochemical cell filled with a solution of 10^{-3}M methylene blue and 0.1M KCl in 50% aqueous methanol or 50% aqueous acetonitrile. The 520 nm transient is observed after application of an anodic →

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potential of 0.1V to 0.7V vs Ag/AgCl for a few seconds on a Pt, Au or SnO_2 electrode. The results indicate that methylene blue triplet is the precursor of the species associated with the 520 nm transient and this transient involves interaction of the triplet with electrodeposited dye.

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Photochemical Transients of Electrode Bound Methylene Blue

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ABSTRACT

A 520 nm transient was observed as the result of the interaction of methylene blue triplet with methylene blue bound to an electrode surface. The transient was observed by laser flash photolysis in an outgassed thin layer transparent electrochemical cell filled with a solution of 10^{-3} M methylene blue and 0.1 M KCl in 50% aqueous methanol or 50% aqueous acetonitrile. The 520 nm transient is observed after application of an anodic potential of 0.1V to 0.7V vs Ag/AgCl for a few seconds on a Pt, Au or SnO_2 electrode. The results indicate that methylene blue triplet is the precursor of the species associated with the 520 nm transient and this transient involves interaction of the triplet with electrodeposited dye.

We wish to report observation of the 520 nm transient absorption in methylene blue solutions as a result of the interaction of methylene blue in the triplet state with methylene blue bound to an electrode surface. Although this spectral transient has been generated earlier via homogeneous processes,[1-5] this is the first time it has been generated through a heterogeneous process.

The transient was observed in a thin layer transparent electrochemical cell filled with a solution of 10^{-3} M methylene blue and 0.1 M KCl in 50% aqueous methanol or 50% aqueous acetonitrile. The same transient appears when the electrode material is Pt, Au or SnO_2 on glass. The optical system permitted monitoring of spectral transients at wavelengths longer than 400 nm beginning approximately 10 μs after the laser flash.

Laser flash photolysis at 667 nm of the outgassed cell adjusted to pH 7.4 generates only the 420 nm transient absorption associated with the methylene blue basic triplet.[6,7] If, however, prior to photolysis, the optically transparent electrode is held at potentials ranging from 0.1V to 0.7V vs Ag/AgCl for a few seconds, a second transient absorption appears at 520 nm. This 520 nm transient appears approximately 10 μs after the flash, as the 420 nm transient of the basic triplet begins to disappear, and its maximum intensity is reached at 25-30 μs which corresponds closely with the half-life of the methylene blue basic triplet. These results indicate two important aspects of the formation of the 520 nm transient. First, at pH 7.4, the methylene blue basic triplet is the precursor of the species associated with the 520 nm transient. Second, generation of the 520 nm transient involves interaction of the triplet with the electro-deposited dye.

If the experiment is performed at pH 2, the 520 nm transient again appears approximately 10 μs after the laser flash, although the intensity is reduced by ca 50%. Instrumental limitations prevent direct observation of the decay of the

methylene blue acidic triplet (λ_{max} ca 375 nm), but it appears that under these conditions the precursor of the species associated with the 520 nm transient is the acidic triplet. The pKa of the methylene blue acidic triplet is 6.8[1,6], so that at pH 2, the major triplet species is the acidic triplet. Thus, both the acidic triplet and the basic triplet can generate the 520 transient absorption.

It is also clear that photoexcitation of methylene blue to the triplet state must occur in solution for observation of the 520 nm transient. If, after electrodeposition of methylene blue, the cell is flushed with methanol and filled with electrolyte which does not contain methylene blue, flash photolysis does not yield the 520 nm transient. Refilling the cell with fresh electrolyte containing methylene blue restores the 520 nm transient to its initial intensity. This reinforces the observation that once methylene blue is electrodeposited, applied potential is not necessary for observation of the 520 nm transient.

The essential spectral characteristics of the 520 nm transient we have observed closely approximate those of the transient generated by homogeneous photolysis of methylene blue solutions with and without oxidizing agents. In addition to the same λ_{max} value, both species exhibit essentially the same molar absorptivity. As estimated from the decreases in the ground state absorbance of methylene blue at 610 nm and the corresponding absorbance of the 520 nm transient 250 μs after the flash, the molar absorptivity of the transient species in our experiment is 1.1×10^5 at 520 nm. The excellent agreement between this value and the value of 1.2×10^5 reported by Danziger, et. al.[1] suggests that the species associated with the 520 nm transient in our experiment is closely related to the species associated with the homogeneously generated transient. Further, the 520 nm transient is not observed when H_2O is the solvent, indicating that initial absorption is by methylene blue monomer.

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